Bulletin of Electrochemistry 15 (5-6) May-June 1999, pp 211-214

0256-1654/99/$ 3-50

ELECTRODEPOSITION OF Ni-Fe-P ALLOY

MALATHY PUSHPAVANAM AND VAIJAYANTHY*

Central Electrochemical Research Institute, Karaikudi 630 006. INDIA
* Regional Engineering College, Trichy 620 015. INDIA

Nickel-iron alloy electrodeposits are of particular interest in the electronic industry especially in the magnetic recording field. However, during deposition, control of iron content is difficult, as it gets altered even with slight changes in operating conditions. Presence of hypophosphite ion can control the iron codeposition by changing the deposition mechanism. Moreover, phosphorous content in deposit can bring about an amorphous structure which incidentally improves the hardness, wear resistance and other magnetic properties of the coating. The results are discussed in this paper.

Keywords: Nickel-iron alloy, hardness, wear resistance, magnetic properties

INTRODUCTION

The electrodeposition of nickel iron alloy is of great practical interest in connection with its use as thin magnetic films for computer memory devices. Binary alloys containing 81% nickel and 19% iron have been promising for high speed magnetic film memories since these films exhibit negligible magnetostrictive effects. Recently the deposition of Ni-Fe-P alloy is receiving [1] interest due to the unique properties offered by the coating. An attempt has been made to deposit this alloy electrolytically and the results are presented in this paper.

EXPERIMENTAL

Six different electrolytes as given in Table I were used to produce alloys of different composition. The electrolytes were prepared by dissolving the nickel salts and sodium acetate in distilled water, purifying the solution in the conventional manner to remove the organic and inorganic impurities [2]. Iron salt and sodium hypophosphite of the required quantities were then added and the *p*H of the solution was adjusted electrometrically.

A dual anode system was used. Stainless steel cathodes of 2 x 5 cms size with an effective plating area of 2 x 2 cm on one side were used for electrodeposition after a suitable etching treatment [3]. Deposits obtained on stainless steel substrates were used for estimating the alloy composition after dissolution of the deposit in a suitable medium. Deposites of 6-8 μm thickness, prepared on copper substrates were used for property evaluation.

Iron and phosphorous in the alloy were estimated by EDTA method and calorimetric method respectively.

The cathode efficiencies for the individual metal depositions were estimated in the conventional method [4]. Hardness of

TABLE I: Various bath compositions used for study

No	Bath composition g/l		Hypo phosphite g/l	Iron sulphate g/l	*p*H	Temp K	C.D. A/dm^2
1a	Nickel sulphate	75	10	15	2	333	2
	Nickel chloride	75					
	Sodium acetate	10					
1b	Nickel sulphate	75	20	15	2	333	2
	Nickel chloride	75					
	Sodium acetate	10					
1c	Nickel sulphate	75	30	15	2	333	2
	Nickel chloride	75					
	Sodium acetate	10					
1d	Nickel sulphate	75	40	15	2	333	2
	Nickel chloride	75					
	Sodium acetate	10					
2a	Nickel sulphate	150	20	5	2	333	2
	Sodium acetate	10					
2b	Nickel sulphate	150	20	10	2	333	2
	Sodium acetate	10					

(Table I continued)

TABLE I: Various bath compositions used for study (Continuous)

No	Bath composition g/l		Hypo phosphite g/l	Iron sulphate g/l	*p*H	Temp K	C.D. A/dm^2
3a	Nickel sulphate	150	20	25	2	333	2
	Sodium acetate	10					
3b	Nickel sulphate	150	30	25	2	333	2
	Sodium acetate	10					
3c	Nickel sulphate	150	40	25	2	333	2
	Sodium acetate	10					
4a	Nickel sulphate	25	20	5	2	333	2
	Sodium acetate	10					
4b	Nickel sulphate	25	20	5	2	333	2
	Sodium acetate	10					
4c	Nickel sulphate	25	30	5	2	333	2
	Sodium acetate	10					
5a	Nickel sulphate	20	10	10	2	333	2
	Sodium acetate	10					
5b	Nickel sulphate	25	10	5	2	333	2
	Sodium acetate						
6a	Nickel sulphate	50	20	15	2	333	2
	Nickel chloride	50					
	Sodium acetate	10					
6b	Nickel sulphate	50	20	15	2	318	2
	Nickel chloride	50					
	Sodium acetate	10					
6c	Nickel sulphate	50	20	15	2	306	2
	Nickel chloride	50					
	Sodium acetate	10					
6d	Nickel sulphate	50	20	15	2	333	2
	Nickel chloride	50					
	Sodium acetate	10					
6e	Nickel sulphate	50	20	15	2	333	3
	Nickel chloride	50					
	Sodium acetate	10					
6f	Nickel sulphate	50	20	15	2	333	4
	Nickel chloride	50					
	Sodium acetate	10					
6g	Nickel sulphate	50	20	15	2	333	2
	Nickel chloride	50					
	Sodium acetate with stirring	10					
6h	Nickel sulphate	50	20	15	2	333	2
	Nickel chloride	50					
	Sodium acetate	10					
	Saccharin	1					
6i	Nickel sulphate	50	20	15	2	333	2
	Nickel chloride	50					
	Sodium acetate	10					
	Saccharin	2					

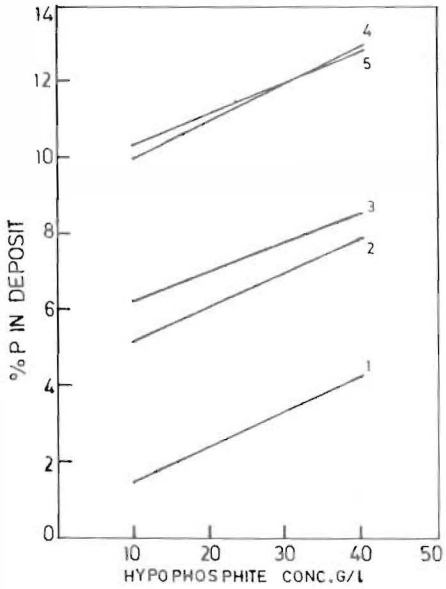

Fig. 1: Effect of hypophosphite concentration on the P content of the deposit

the deposites was determined by the Vicker's indentation method at a load of 20 gms.

RESULTS & DISCUSSION

The electrodeposition of phosphorous alloys is of special interest for several years. Phophorous is a non-metal and a nonconductor of electricity and has not been electrodeposited alone from aquous solutions. Only iron group metals have been shown to be effective in inducing codeposition of phosphorous.

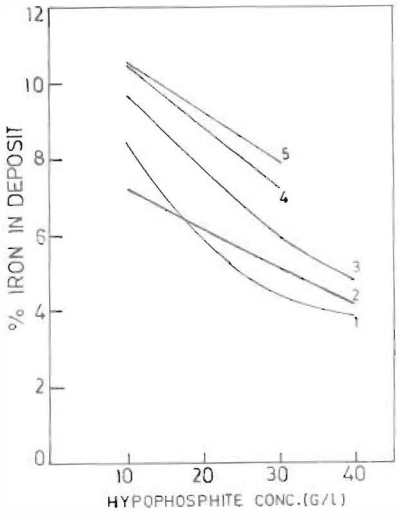

Fig. 2: Effect of hypophosphite concentration on the Fe content of the deposit

Figs. 1 and 2 show the effect of hypophosphite concentration on the phosphorous and iron contents of the deposites obtained from baths I-V. It is observed that the iron and phosphorous contents of the deposites are higher when deposited from a sulphate bath than from a sulphate-chloride bath, particularly at low current densities. This is in accordance with the behaviour of nickel-iron baths. Hence, it appears that phosphorous codeposition is favoured under conditions that favour iron codeposition. In dilute solutions, viz., baths IV and V, where the Ni/Fe ratio is much less compared to baths I-III, both iron and phosphorous contents of the deposites are higher.

As per the mostly accepted theory of nickel iron alloy codeposition [5], the process occurs through the adsorption of hydroxide species. The adsorbed iron hydroxide forms at a lower surface *p*H and gets reduced at a faster rate compared to the adsorbed nickel species. The increse in phosphorous content with iron indicates that the latter is a better inducer to cause the codeposition of phosphorous than nickel.

Generally, nickel-iron alloy deposition belongs to the anomalous type wherein the less noble metal deposites in preferance. However, the relation between the iron content of the alloy in the deposit to its ratio in the solution, as in Fig. 3, shows that the system belongs to the normal type. The iron contents of the alloy obtained from all the five solutions, are always lower than the composition referance line.

It has been mentioned in the literature, that presence of certain additives like thiurea and silica are capable of altering the kinetics of codeposition from anomalous to normal [6-8].

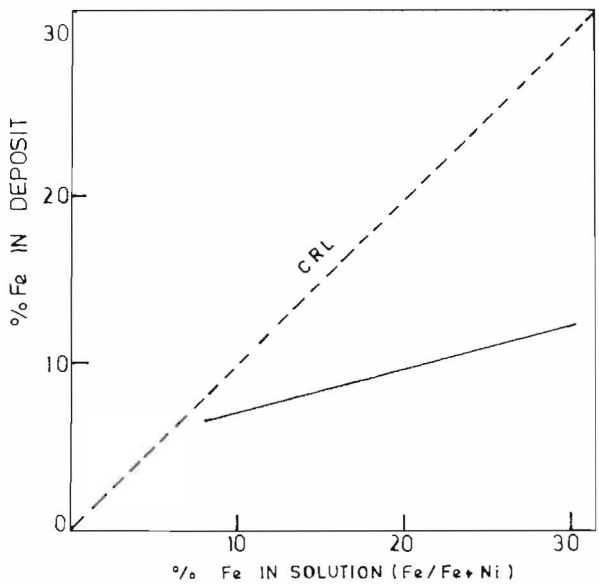

Fig. 3: Effect of Fe content in solution on that IN deposit

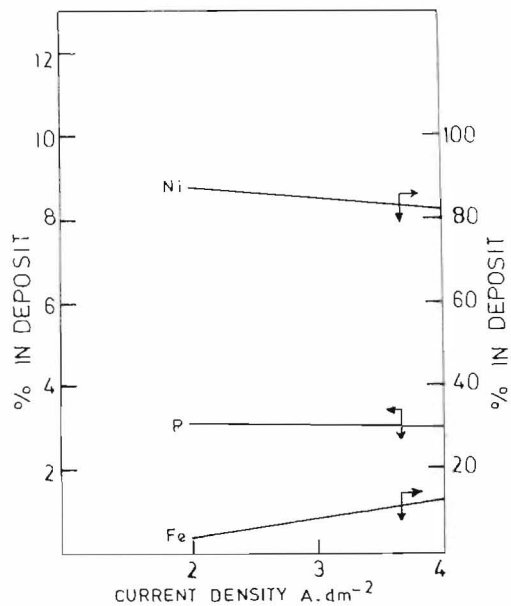

Fig. 4: Effect of current density on the alloy composition

These additives get adsorbed at the cathode and inhibit iron deposition. In a similar manner, the normal behaviour observed in this system should be attributed to the presence of hypophosphite ion. According to [9] this effect would be due to suppression of the rate of iron deposition or enhancement of nickel deposition. It is reported [10] that a overall reduction in the iron content in the presence of relatively small amounts of hypophosphite. It is suggested [11] that phosphorous was adsorbed at the cathode to form a phosphorous nickel complex which is discharged at a more noble potential than nickel alone. Hence,it can be concluded

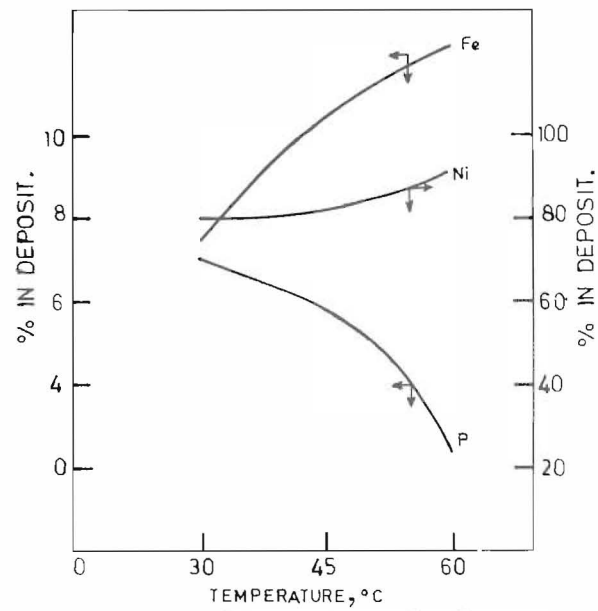

Fig. 5: Effect of bath temperature on the alloy compositon

TABLE II: Cathode current efficiencies of alloy deposition from different baths

Bath	C.E %	Bath	C.E %	Bath	C.E. %	Bath	C.E. %
1a	60.94	3a	62.23	5a	42.32	6e	67.24
1b	62.92	3b	52.83	5b	33.46	6f	65.57
1c	66.76	3c	46.35	6a	70.25	6g	59.77
1d	77.30	4a	42.32	6b	60.29		
2a	63.62	4b	28.50	6c	55.52		
2b	66.68	4c	22.92	6d	92.02		

that the presence of hypoposphite ion favours the deposition of nickel and change the codeposition nature from anomalous to normal.

Figs. 4 and 5 indicate the influence of parametric variables on the alloy composition. Iron content showed a slight increase while phosphorous content remained unaffected with increase in current density. Higher solution *p*H resulted in higher iron content of the alloy, but caused a reduction in its phosphorous content.

A reduction in the phosphorous content and increase in the iron content were observed with increase in the solution temperature along with an overall increase in the total efficiency of the deposition. Deposition under stirred conditions helped in incresing both the iron and phosphorous content of the alloy, but reduced the cathode efficiency. Presence of saccharine in the bath, similar to nickel-iron alloy deposition decreased the iron content of the alloy without appreciably altering its phosphorous content.

The cathode current efficiency of alloy deposition, as given in Table II, varied widely with the change in the operating conditions. Highest plating efficiencies were obtained from baths operated at elevated temperatures and at high *p*H values. By comparing the data, it is understood that an increase in phosphorous content, generally resulted in a decrease in iron deposition efficiency but,increased the overall alloy deposition efficiency. It was also observed that in a sulphate-chloride bath, the overall efficiency is slightly low, may be because of low solution *p*H. Low metal ion concentration resulted in a loss of efficiency but, increased the phosphorous content of the alloy. Solution stirring

TABLE III: Hardness values of alloy deposits

% P	% Fe	Hardness, VHN
3.27	7.50	221.4
3.27	10.38	246.5
5.00	12.20	353.0

increased the iron and phosphorous deposition efficiency but, reduced the ovarall efficiency. Microhardness of the alloy deposites, as given in Table III, are dependant on phosphorous and iron contents. At same phosphorous content, hardness was decided by the iron content of the alloy. Very high phosphorous content resulted in reduction in hardness.

CONCLUSION

Ni-Fe-P alloys can be produced successfully by electrodeposition technique.

REFERENCES

1. Malathy Pushpavanam, V Raman and B A Shenoy, *Corr Bull*, **3** (1983) 322
2. F Lowinheim, *Modern Electroplating*, III Ed, John Wiley & Sons Inc, New York (1974)
3. N V Parthasarathy, Practical Electroplating Handbook, Prentice Hall, Englewood Cliffs, NJ, (1989)
4. A Brenner, *Electrodeposition of alloys*, Acadamic Press , NY (1963)
5. J Horkins, *J Electrochem Soc*, **128** (1981) 45
6. Jersy Bielinski and Jan Przyluski, *Surf Technol*, **9** (1979) 65
7. J R Roos, J P Celes, J Fransaer and C Buellens, *J Metal*, **11** (1990) 60
8. H M Wang and T G O'Keef, *Plat & Surf Fin*, **83** (1995) 149
9. K Sridhar and K Sheppard, *Trans Inst Met Finish*,, **72** (1994) 153
10. W O Freitag, J S Mathias and G Diguilio, *J Electrochem Soc*, **111**, (1964) 35
11. T Atanasin, A Kalisaru and M Popeseu, *Chem Abst*, **59** (1959) 15815b